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ADVANCED DOUBLE LAYER CAPACITOR

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1. TECHNICAL OBJECTIVES

The overall goal of this project is to develop electrochemical capacitors utilizing an electrode-solid ionomer electrolyte composite. An advantage of these devices over conventional double layer capacitors would be the absence of free liquid electrolyte and thus greater safety and reliability.

In the second quarter, we have continued our efforts on Task IA of the Work Plan. Specifically we have 1) fabricated noble metal oxides of the RuO_x type into electrodes, 2) formed metal oxide-Nafion electrode composites, 3) integrally bonded Nafion membranes to composite electrode structures, 4) constructed electrode holders for properly gasketing these electrodes during testing, and 5) begun to set up an AC impedance test system for characterizing the response of these electrodes.

2. EXPERIMENTAL METHODS

2.1 Preparation of Materials

2.1.1 Ti Substrates: The Ti substrate has some native titanium oxide present. This is desirable on the metal oxide side of the electrode, but can cause problems on the ohmic contact side (the titanium oxide is poorly conducting). One side of a Ti sheet or both sides of a Ti screen are plated with gold in an immersion bath (U.S. Patent 3,891,447). This method gives a light plate of gold on Ti.

2.1.2 Noble Metal Oxides: Preparation of oxide spraying $RuCl_3$ on a Ti substrate and decomposing were done as reported in the 1st Quarterly Report. Roughening the substrate with sandpaper produced a more adherent RuO_x deposit.

To prepare RuO_x in particulate or powder form a "Thermal Method" based on the oxidative decomposition of Ru salt at elevated temperature was used.

2.1.3 Ionomers: Nafion 117 used for impregnation of electrodes was purchased as a 5% solution in alcohol-water from Aldrich Chemical. Except for dilution, it was used without further treatment.

Nafion 117 in sheet form was pretreated before being bonded to electrodes. The dry membrane was boiled in distilled water for 30 minutes and then exchanged in 1.2N HCl for 30 minutes. After rinsing, the membrane was again boiled for 30 minutes in water. The membrane was then exchanged two times in 1.5N H_2SO_4 (30 minutes each time). After rinsing, the membrane was given a final equilibration in boiling water for 30 minutes.

2.1.4 **Ionomer Impregnation**: Two methods of forming the electrode-ionomer composite were used in the 2nd Quarter. The first one involved mixing powder, prepared by the "Thermal Method" with a Nafion 117 solution. The 5% stock solution was diluted with 50% isopropyl alcohol/water. An appropriate amount of solution was added to the powder so as to make 15 wt% Nafion in the final electrode. The mixture was processed to obtain homogeneity and dried.

The second method deposits RuO_x directly in and on the substrate of a Nafion 117 membrane by adapting a published procedure (1). The membranes were swelled in a methanol/water solution and then exchanged with $RuCl_3$. The RuO_x was precipitated by imbibing the membrane with a KOH solution.

2.1.5 **Electrode Preparation**: A gold-plated Ti screen was sprayed lightly on both sides with 10% FEP. The screen was then placed on a sheet of 1 μm porosity Gore-Tex and sintered. Teflon was mixed with the electrode (or electrode-ionomer) powder. Typically, 25 wt% Teflon was used. The catalyst-Teflon mixture was deposited on the screen; sintered; and pressed at elevated pressure. After pressing, the Gore-Tex backing was removed.

Some electrodes were bonded to hydrated Nafion 117 membranes at elevated temperature and pressure. After cooling, the membrane and electrode were immediately removed and soaked in distilled water.

2.2 Electrochemical Testing

Electrodes were tested in 1M H_2SO_4. For membrane-bonded electrodes, the membrane faced the solution. A Luggin capillary led to a bridge which contained a $Hg/HgSO_4$ electrode. The height of the electrode above the tip of the capillary could be adjusted by a Teflon screw. The counterelectrode was a Pt sheet which covered the bottom of the cell so as to provide an even current distribution on the working electrode.

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3. RESULTS AND DISCUSSION

3.1 Electrode Testing

Five types of electrodes have been tested: 1) RuO_x thermally decomposed from $RuCl_3$ on a Ti sheet, 2) thermally prepared RuO_x-Teflon bonded to a Ti screen, 3) electrodes of Type 2 bonded to a Nafion 117 membrane, 4) electrodes of Type 2 impregnated with Nafion and bonded to a Nafion 117 membrane, and 5) electrodes with RuO_x deposited directly into a Nafion 117 membrane.

Cyclic voltammograms of Type 1 electrodes were shown in the 1st Quarterly Report. **Figure 1a** shows a voltammogram of a Type 2 electrode. This electrode was prepared at a loading of 10 mg/cm² on a bare Ti screen (not gold plated). No well resolved peaks are seen, but when current at 0.1 V was plotted vs. sweep rate (**Figure 1b**), the plot is linear. A capacitance of about 28 mF/cm² is derived. This is twice the value seen for the Type 1 electrodes.

Figure 2a shows a typical voltammogram of a Type 3 electrode. A gold-plated screen was used. The peaks are well resolved. **Figure 2b** shows a plot of current vs. sweep rate. When the membrane was bonded to the screen side, capacitances of about 60 mF/cm² were obtained.

Next Nafion-impregnated electrodes were prepared. The loading was 20 mg/cm² of RuO_x + Nafion. **Figure 3a** shows the voltammogram. The voltammogram has a flatter shape than that of the Type 3 electrode. **Figure 3b** shows the plots of current density vs. sweep rate. The plots are not as linear as the plots for the other type electrode. Approximate values of capacitances were similar to those of Type 3 electrodes.

Figure 4 shows a voltammogram of a Type 5 electrode. No well resolved peaks are seen and the voltammogram is tilted. Good ohmic contact to the current collector was not being made. No quantitative information could be derived from these voltammograms.

The above results show that it is feasible to fabricate RuO_x electrodes from RuO_x powder. High values of capacitance can be obtained. When the ohmic current collector screen is properly prepared, similar voltammograms to those obtained from Type 1 electrodes are obtained. Thus, the chemical and capacitative processes are probably similar in the two types of electrodes.

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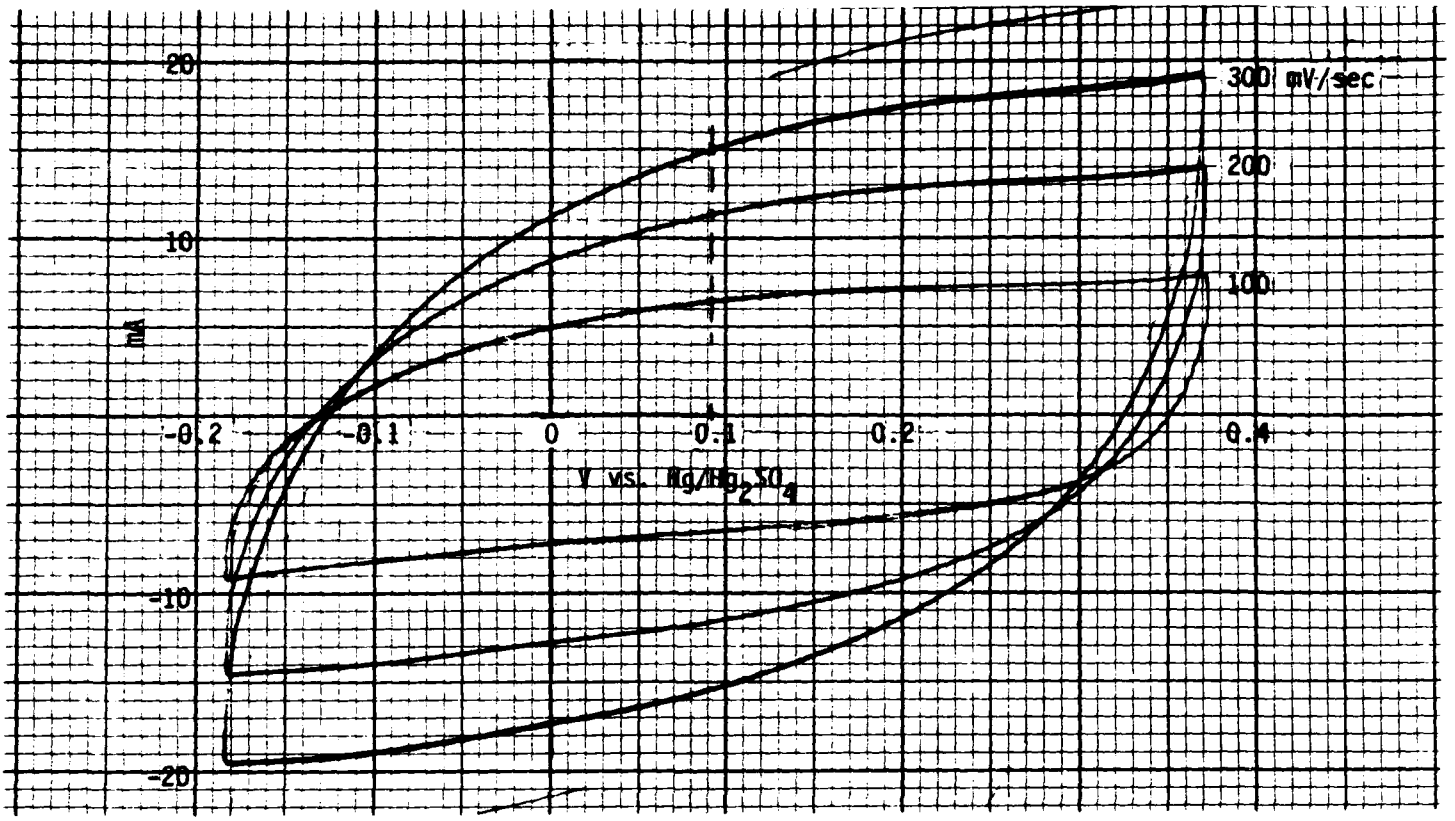
a) Voltammogram in 1M H_2SO_4 Under an N_2 Atmosphere



b) Current Density at 0.1 V vs. Sweep Rate

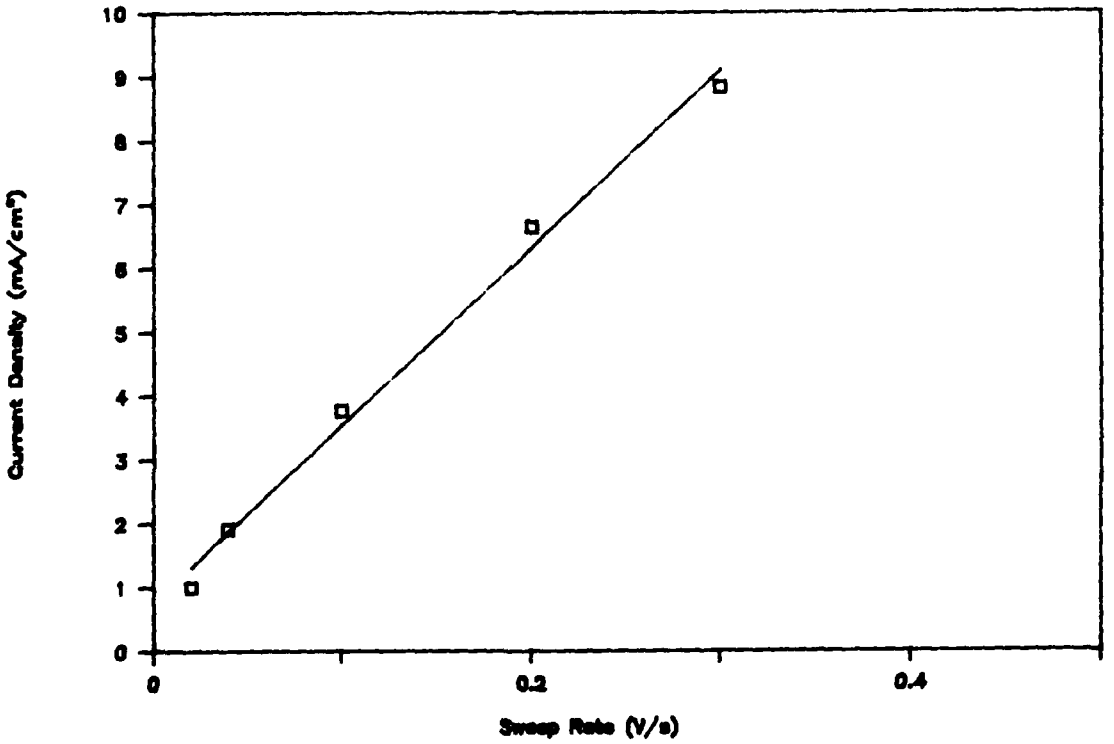
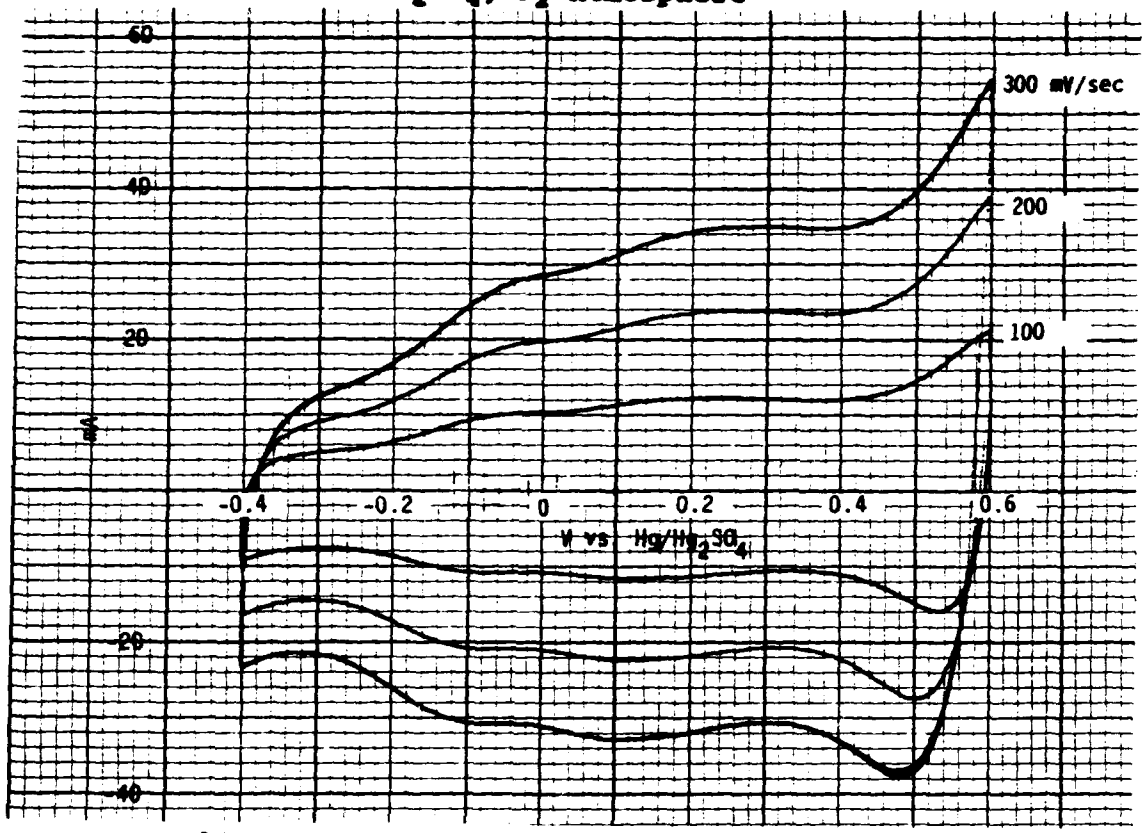


Figure 1: RuO_x Supported on a Bare Ti Screen

a) Voltammogram with Membrane Face in Contact with 1M H_2SO_4, N_2 Atmosphere



b) Current Density at 0.1 V vs. Sweep Rate

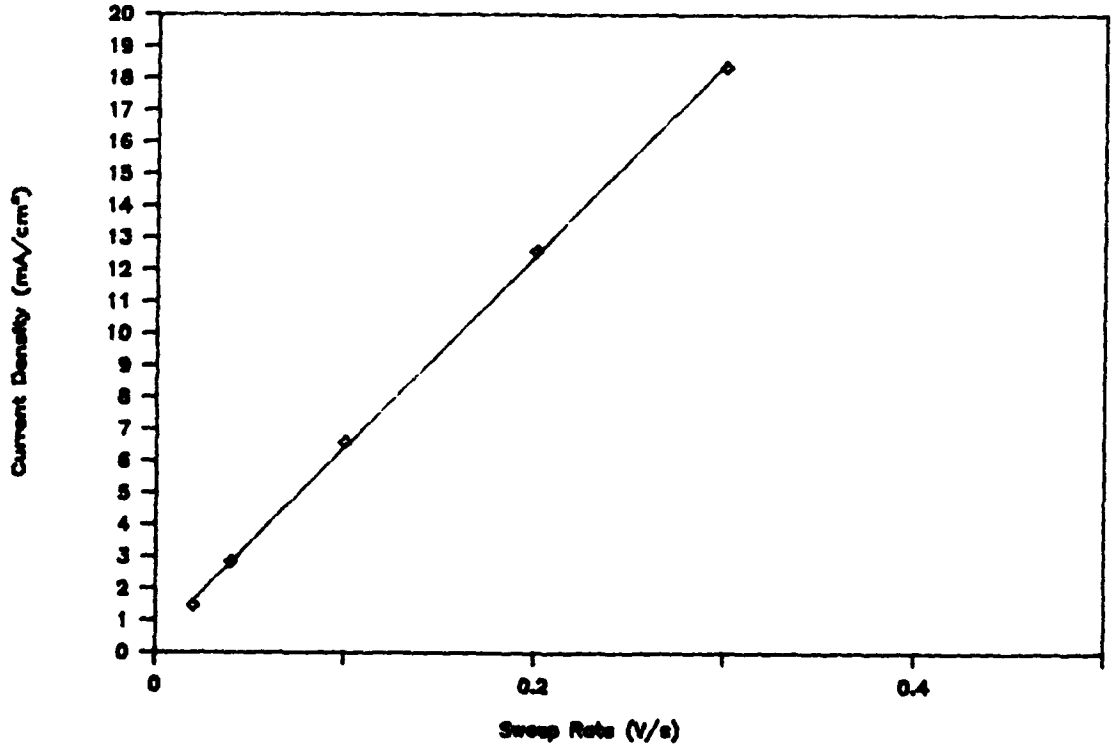
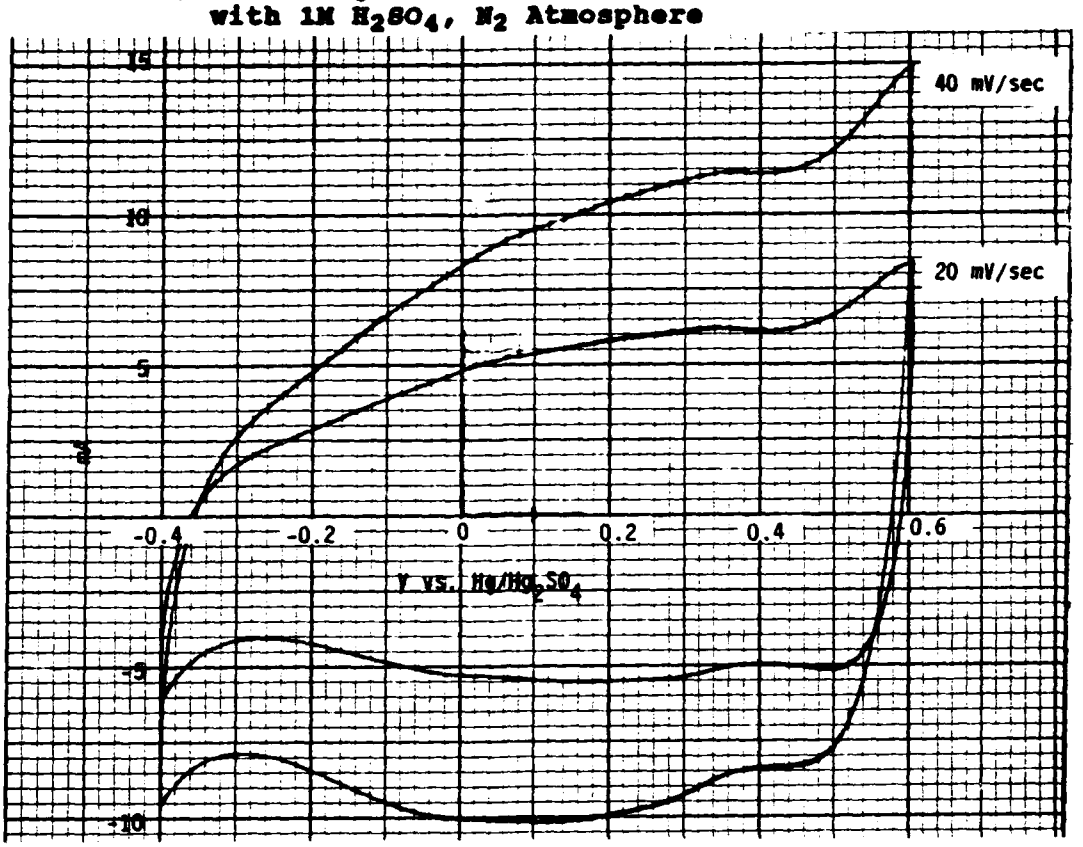


Figure 2: RuO_x on a Gold-Plated Ti Screen and Bonded to a Nafion 117 Membrane

a) Voltammogram with Membrane Face in Contact with 1M H_2SO_4, N_2 Atmosphere



b) Current Density at 0.1 V vs. Sweep Rate

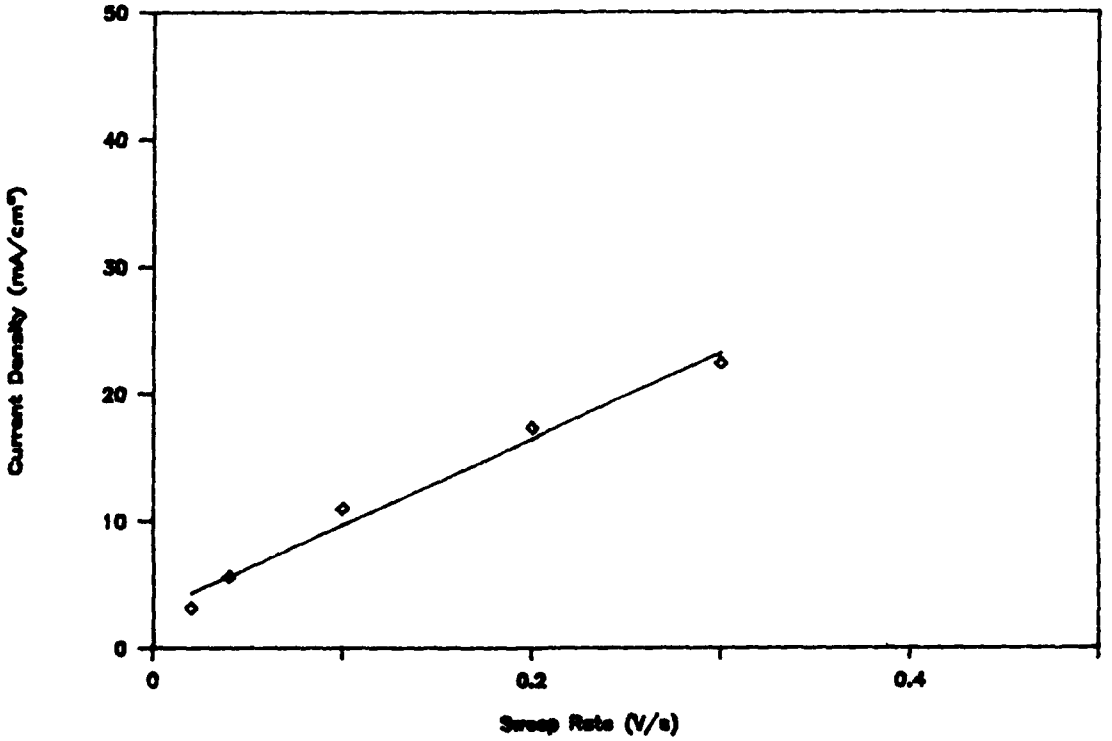


Figure 3: RuO_x-Nafion Impregnated on a Gold-Plated Ti Screen and Bonded to a Nafion 117 Membrane

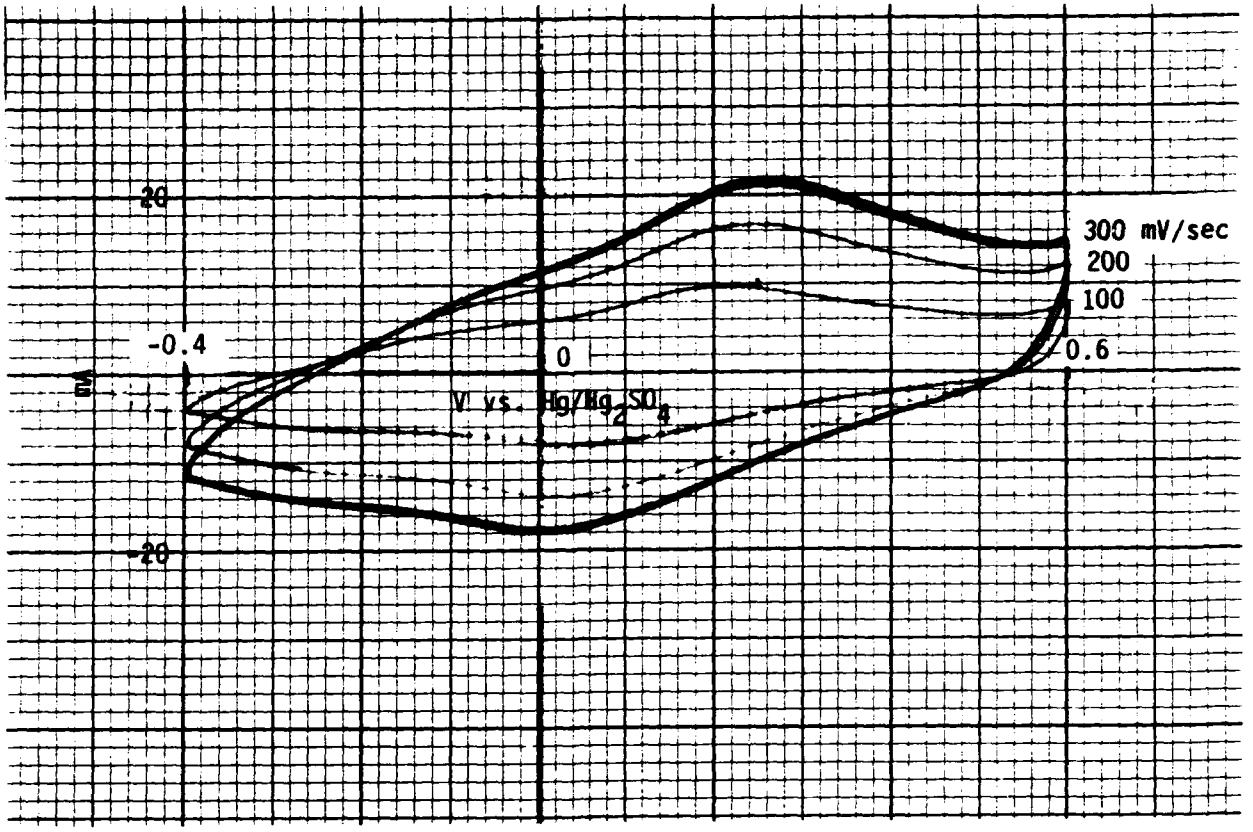


Figure 4: RuO_x Deposited in a Nafion 117 Membrane; Voltammogram in 1M H_2SO_4

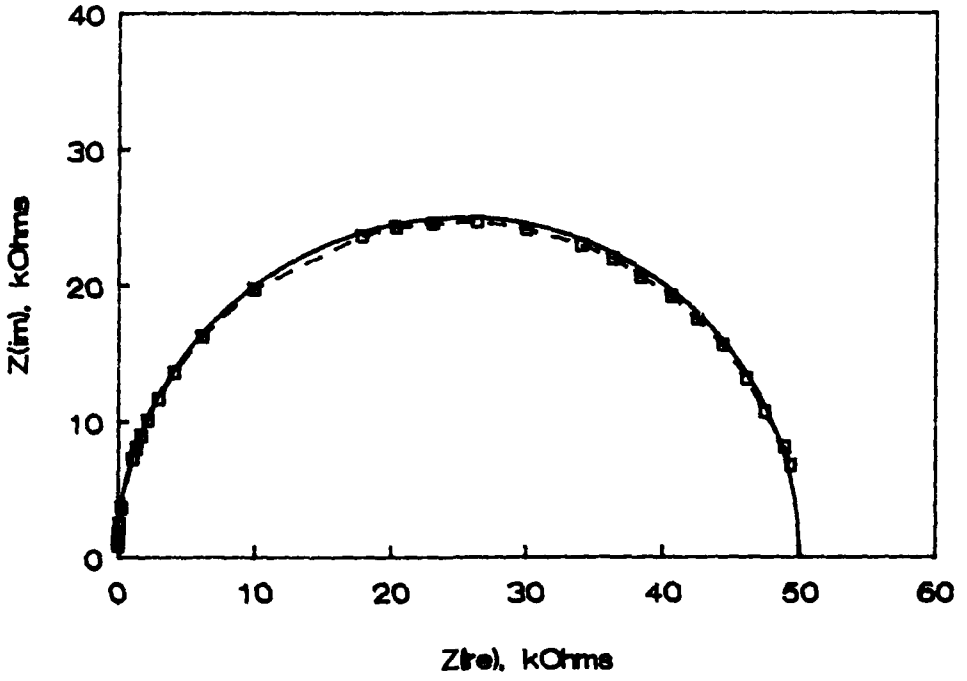


Figure 5: Nyquist Plot of Equivalent Circuit Containing a 20 nF Capacitor in Parallel with a 50 kΩ Resistor

The electrodes bonded to the Nafion membrane gave similar values of capacitance to those exposed directly to the sulfuric acid electrolyte. H_2SO_4 and H_2O are probably transported through the membrane and partially wet the electrode. Thus, effective surface area and capacitance will be higher than what would be expected if just a surface layer of the electrode was in contact with the Nafion membrane.

3.2 Impedance Measurements

Measurement of the impedance electrode-electrolyte interface represents a way to obtain accurate capacitance values over a range of DC bias voltages. A small AC voltage is superimposed on the DC bias voltage and the magnitude and phase shift of the resulting current are determined. Several instrumental methods are available for this determination (2). The lock-in amplifier technique represents a way to get accurate measurements of the magnitude and phase angle of the current at frequencies of 5 Hz to 100 kHz.

A PAR 5210 lock-in amplifier was acquired and interfaced to an existing PAR 173/276 potentiostat. An equivalent circuit was used to test the instrumentation. It consisted of a 20 nF capacitor in parallel with a 50 kΩ resistor. The experimental Nyquist plot is shown in **Figure 5**, along with the theoretical curve. There is excellent agreement between theory and experiment for the equivalent circuit.

4. FUTURE WORK

When the AC impedance system is fully operational, we expect to use this system to obtain quantitative information about the electrode-ionomer interface. RuO_x-type materials will continue to be emphasized. The optimum methods of forming the electrode-ionomer composites will be investigated. Other materials, such as RuO_x on carbon, carbon, and high surface area metals, will be studied to quantify their electrochemical behavior.

5. REFERENCES

1. A. Michas, J.M. Kelly, R. Durand, M. Pineri, and J.M. D. Coey, "Preparation, Characterization and Catalytic Properties of Perfluorosulfonated Ion-Exchange Membranes Containing Surface-Concentrated, Hydrated Ruthenium Oxide Particles," *J. Membr. Sci.*, **29**, 239 (1986).

2. A.J. Bard and L.R. Faulkner, Electrochemical Methods, New York, John Wiley and Sons, 1980, Chapter 9.